UNION CARBIDE

FIRST QUARTERLY REPORT

SECONDARY ZINC-OXYGEN CELL FOR SPACECRAFT APPLICATIONS

(23 JUNE, 1966 - 23 SEPT., 1966)

CONTRACT NO.: NAS-5-10247

for

GODDARD SPACE FLIGHT CENTER
GREENBELT, MARYLAND

Prepared by

UNION CARBIDE CORPORATION
CONSUMER PRODUCTS DIVISION
RESEARCH LABORATORY - PARMA, OHIO

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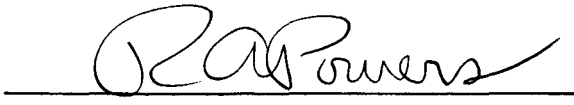

R. A. Powers, Director

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RESEARCH LABORATORY
PARMA, OHIO

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ABSTRACT

Development of a 16 AH unit zinc-oxygen test cell has been completed during the first quarter covered by this report. The ampere hour rating is based upon the 19.2 grams of zinc actually used in the first test cells and represents the calculated theoretical capacity. Optimization of these cells will be carried out in further work. "Lucite" has been used as the material of construction to permit visual observation of the wetproof back side of the "fixed-zone" oxygen electrode as well as the two electrolyte chambers on either side of the charging electrode during the period of cell cycling.

Characterization of cell performance at the twenty-four hour rate is now in progress using a nickel screen charging electrode. Cell performance studies at the two-hour rate have begun. Characterization of cell rechargeability has also been initiated on a two-hour discharge, six-hour charge cycle. This work has now undergone fourteen complete cycles while cell characterization at the twenty-four hour rate has progressed through the sixth complete cycle. The unit zinc-oxygen cell was also operated at discharge currents ranging up to 6.9 amperes. Performance of the first test cells under these conditions clearly indicated its capability of meeting high rate discharge requirements.

* * *

INTRODUCTION

The technical approach employed in conducting the effort of this quarter is based upon Union Carbide's background experience in fuel cell technology, in the "Air Cell," and in rechargeable battery systems. The zinc-oxygen system was selected as the best system for meeting the requirements of spacecraft applications because of its high theoretical energy density, 541 watt-hours/lb. The state-of-the-art of the primary zinc-oxygen systems for certain applications has now approached 200 watt-hours/lb.

Even with the expected reduction in energy density because of the gas container requirement for conversion of the system from a primary to a secondary battery, the zinc-oxygen system still appears superior to other systems which have a higher theoretical energy density.

The oxygen electrodes employed as a starting point in our present work are the thin "fixed-zone" electrodes developed over a period of years by Union Carbide for fuel cell batteries. The zinc electrodes being used in the initial cells are those that have been developed for use in high rate zinc-oxygen batteries. The feasibility of using inorganic as well as organic separators will also be examined.

Unit cell development was completed during the present quarter. Cell performance was determined at several discharge rate levels. Performance data obtained clearly indicated the zinc-oxygen system's capability of delivering the high rate requirements of spacecraft applications.

DISCUSSION

A. Description of Electrodes

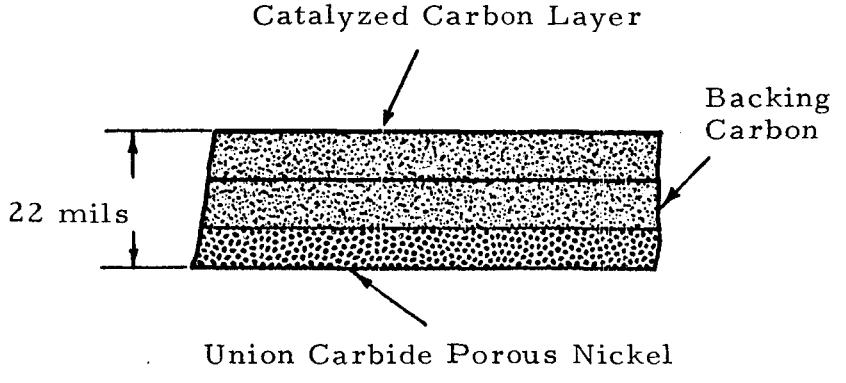
1. Oxygen Electrode

The oxygen electrode employed in the unit cell is of the thin "fixed-zone" type that has been described by Kordesch and coworkers (1-7) in work done by Union Carbide for other Government Agencies, in which the electrochemically active carbon layer is applied to a thin, but strong, porous metal backing. Thus, the structural characteristics of the metal

backing are mated with the electrochemical characteristics of carbon to produce a low-cost, high-performance electrode. This thin electrode is schematically illustrated in Figure 1. The porous nickel backing allows the ready transport of oxygen to the reaction site. However, permeation of electrolyte through the porous nickel is prevented by wetproofing treatment. This electrode does not rely on a sensitive pressure balance with attendant sensor problems to maintain the gas-liquid interphase at an appropriate level in the structure. Rather a stable interphase is an inherent characteristic of such a hydrophobic electrode. As expected, no electrolyte permeation through the electrode to the porous nickel backing has been seen in any of the unit cells built and operated to date.

FIGURE 1

CUT-THROUGH THIN "FIXED-ZONE" ELECTRODES



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2. Zinc Electrode

The zinc electrodes used in the unit cells built to date for this project are those developed within Union Carbide in previous work directed toward both development of the primary zinc-oxygen battery system and rechargeable zinc electrodes. Work conducted prior to the present contract efforts has shown that such an electrode is capable of successful performance at current drains at least as high as those represented by the two-hour discharge rate of the present spacecraft applications.

B. Unit Cell

1. Unit Cell Construction

The construction of the unit cells built is that shown schematically in Figure 2 and described in detail in Table I. "Lucite" was purposely selected as the material of construction of the unit cell body so that it would be possible to visually observe the back of both the oxygen electrode and the zinc electrode as well as to be able to look into the electrolyte chambers of the cell itself during the various phases of cell cycling. An expanded nickel metal screen electrode, serving as the charging electrode, has been interposed between the zinc electrode and the oxygen electrode with appropriate separators. Charging is therefore carried out between this charging electrode and the zinc electrode so that the oxygen electrode can be excluded from the charging circuit.

TABLE I

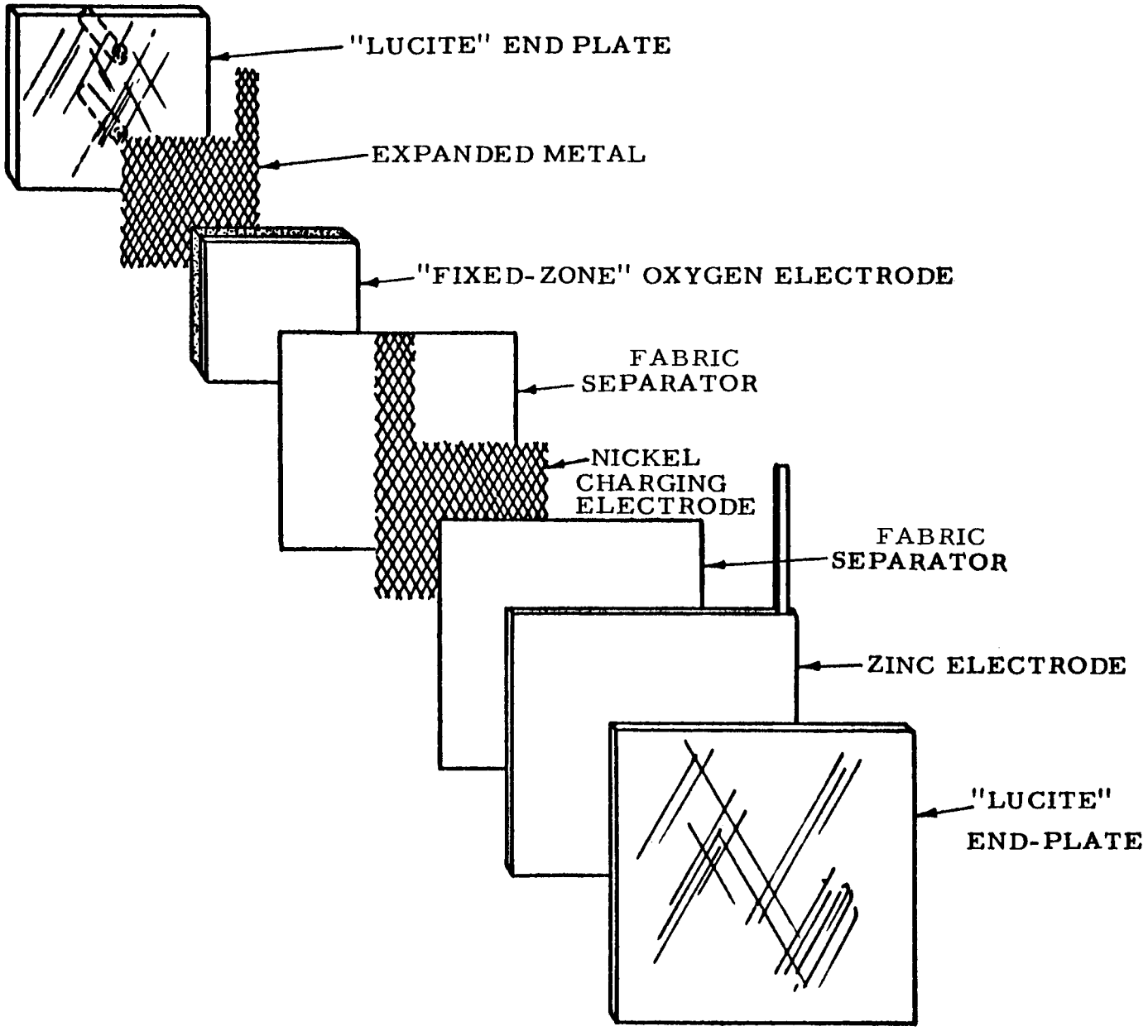
DESCRIPTION OF UNIT TEST CELL

	Dimension	Weight
"Fixed-Zone" Oxygen Electrode	3" x 3" x 0.022"	10 g
Non-Woven Cellulosic Separator	3" x 3" x 0.008"	
Expanded Nickel Metal Charging Electrode*	3" x 3" x 0.020"	2.6 g
Non-Woven Cellulosic Separator	3" x 3" x 0.012"	
Zinc Electrode	3" x 3" x 0.125"	19.2 g
Electrolyte:	Composition	Amount
	38% KOH + 3.5% ZnO	33 ml
Oxygen Source	Oxygen Cylinder	

* Exmet 2/0

FIGURE 2

DETACHED VIEW OF ZINC-OXYGEN UNIT CELL



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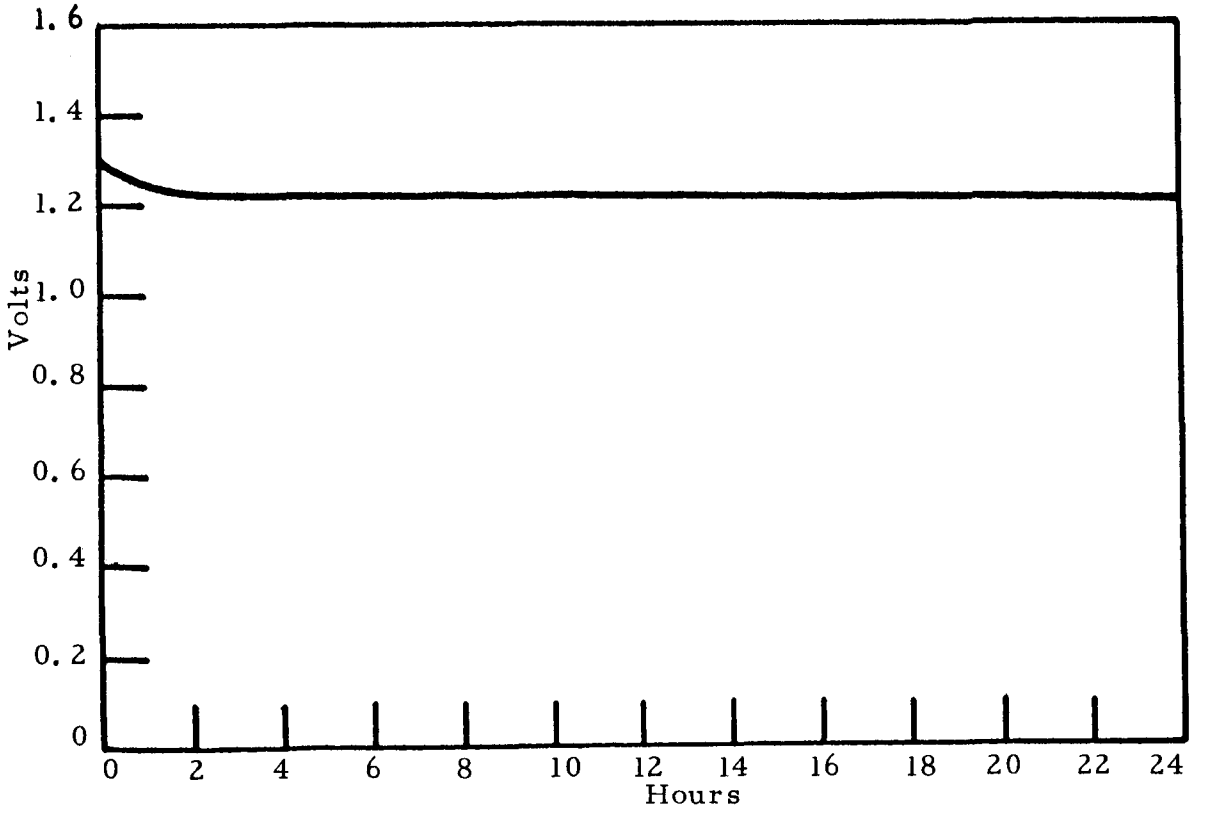
2. Unit Cell Performance

Characterization of the unit cell has been conducted on a twenty-four hour discharge, twenty-four hour charge cycle. This has progressed through the sixth cycle at the present time. Figure 3 shows a typical discharge curve obtained.

FIGURE 3

24-HOUR DISCHARGE OF ZINC-OXYGEN UNIT CELL WITH 0.4 AMPERE CONSTANT CURRENT



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A study of unit cell rechargeability on a two-hour discharge, six-hour charge cycle has also been initiated. Typical performance of the initial unit cell is presented in Table II.

TABLE II

RECHARGEABILITY OF ZINC-OXYGEN UNIT CELL

(2-Hour Discharge, 6-Hour Charge Cycle)

Cycle Number	Discharge (average)			Discharge-Output (Across 0.75Ω for 2 hrs)	Charge-Input (6 hrs at 0.5 amps)
	Voltage	Current	Apparent Current Density		
1	1.17 volts	1.56 amps	26.9 ma/cm²	3.12 amp-hrs	3.00 amp-hrs
2	1.17	1.56	26.9	3.12	3.00
3	1.17	1.56	26.9	3.12	3.00
4	1.14	1.52	26.2	4.94*	3.00
5	1.13	1.51	26.0	3.02	3.00
6	1.13	1.51	26.0	3.02	3.00
7	1.11	1.48	25.5	2.96	3.00
8	1.11	1.48	25.5	2.96	3.00
9	1.10	1.47	25.4	2.94	3.00
10	1.09	1.45	25.1	2.90	3.00
11	1.08	1.44	24.8	2.88	3.00
12	1.07	1.43	24.7	2.86	3.00
13	1.06	1.41	24.3	2.82	3.00
14	1.05	1.40	24.2	2.80	3.00

* Cell was discharged for 3.25 hours

This table shows that the unit cell delivered an average of 1.56 amperes at an average potential of 1.17 volts during the first three discharge cycles for periods of two hours. On the fourth cycle, the cell was allowed to discharge for 3.25 hours and delivered an average current of 1.52 amperes at an average potential of 1.14 volts. Thus, while the depth of discharge of the cell was increased from 3.12 ampere-hours during the first three discharges to 4.94 ampere-hours during the fourth discharge, the average potential at which the

current was delivered dropped only from 1. 17 volts to 1. 14 volts. Subsequent discharges were for a period of two hours each across a fixed resistor of 0. 75 ohm. The ampere-hour output slowly decreased by the fourteenth cycle. On the fourteenth discharge the cell delivered 2. 80 ampere-hours over a period of two hours at an average current of 1. 40 amperes and an average potential of 1. 05 volts. Cell charge input for each cycle was 3. 00 ampere-hours. Graphs of the first, fourth, ninth, twelfth and fourteenth discharges followed by their respective charges are presented in Figures 4-8 inclusive. Oxygen evolved on charge was not contained for discharge. The oxygen source used was a cylinder with a reduction valve. The amount of oxygen used was not measured but should be essentially the theoretical amount required from previous fuel cell experience with this oxygen electrode.

The performance of the unit oxygen-zinc cell has also been evaluated at current drains above those already reported. This work is summarized in Table III below. These data clearly indicate that the oxygen-zinc system is easily capable of meeting the high-rate discharge requirements posed by the spacecraft applications.

TABLE III

PERFORMANCE OF UNIT ZINC-OXYGEN RECHARGEABLE CELL OVER A RANGE OF CURRENT OUTPUT*

Current Output Amperes	Apparent Electrode Current Density ma/cm^2	Sustained Potential Volts**
0. 42	7. 2	1. 29
0. 56	9. 6	1. 26
0. 82	14. 1	1. 23
1. 52	26. 2	1. 14
2. 67	46. 0	1. 00
3. 64	62. 7	0. 91
4. 50	77. 6	0. 84
5. 20	89. 7	0. 78
5. 92	102. 0	0. 74
6. 35	110. 0	0. 68
6. 90	119. 0	0. 64

*This cell discharged successively for 5-minute intervals at each current output level. Total capacity delivered was 3. 2 ampere-hours.

** Voltage at end of each 5-minute interval.

FIGURE 4

1ST DISCHARGE OF ZINC-OXYGEN UNIT CELL

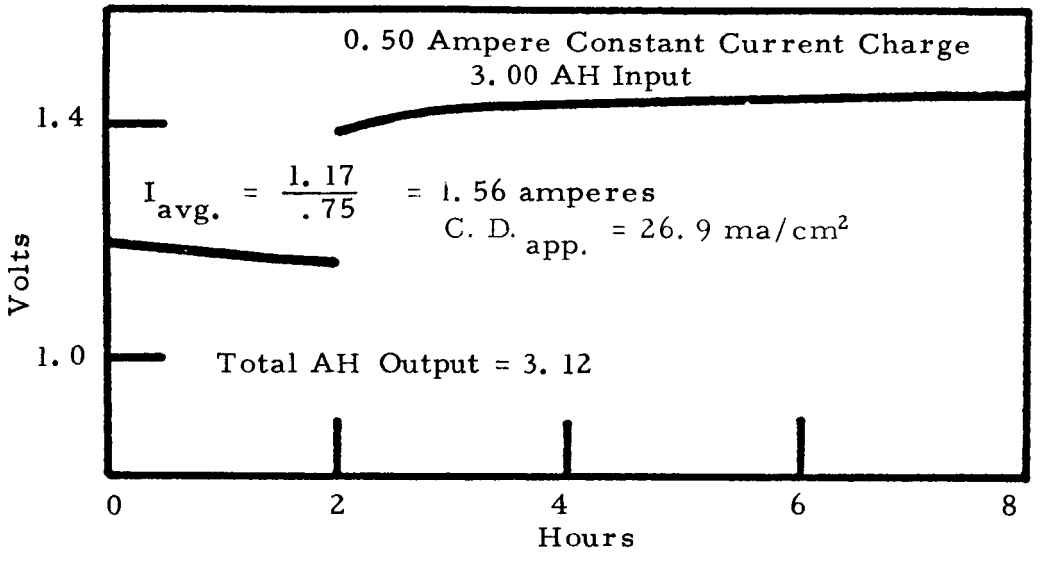

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FIGURE 5

4TH DISCHARGE OF ZINC-OXYGEN UNIT CELL

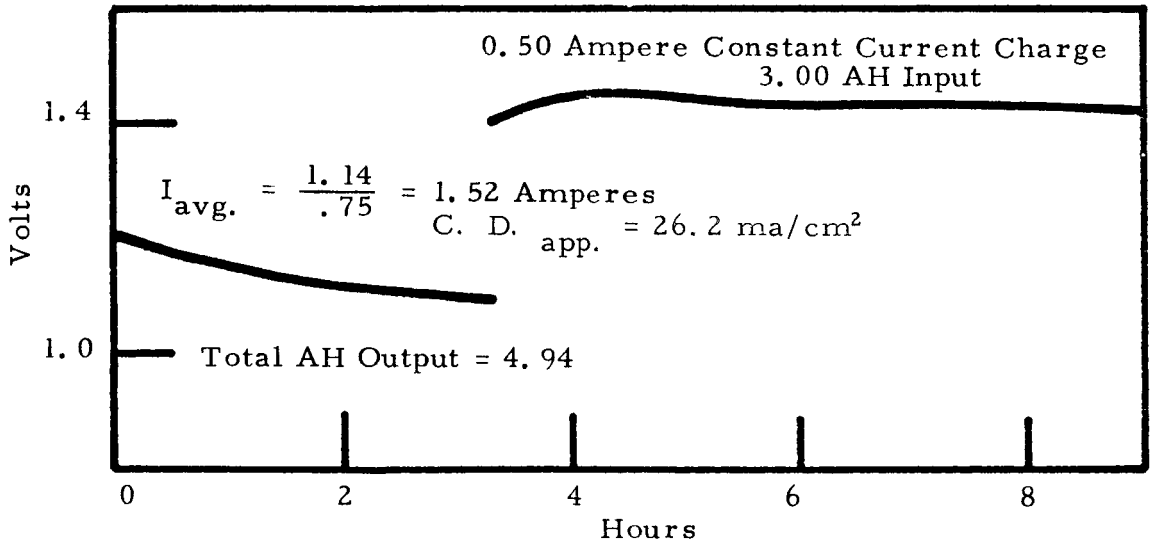

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FIGURE 6

9TH DISCHARGE OF ZINC-OXYGEN UNIT CELL

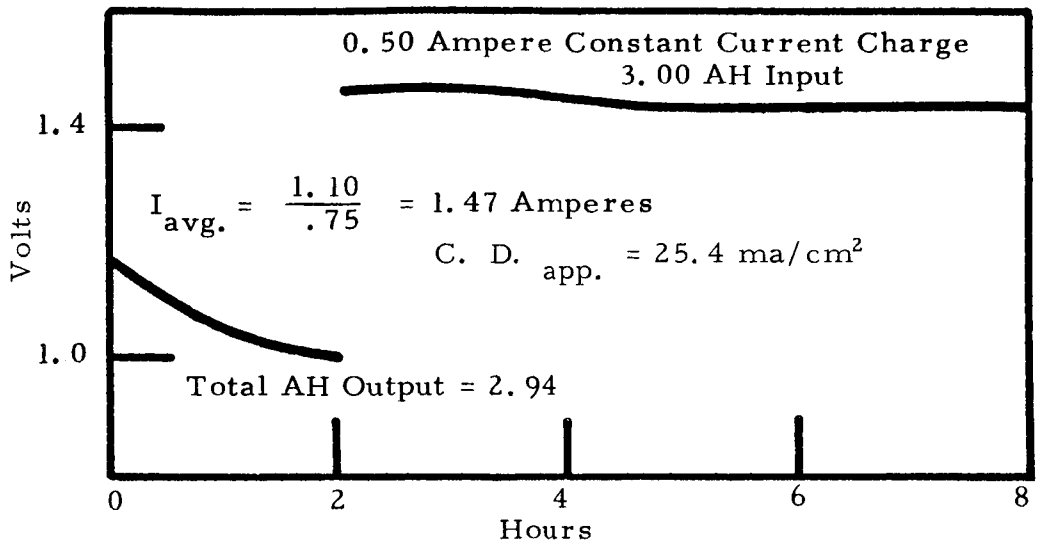

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FIGURE 7

12TH DISCHARGE OF ZINC-OXYGEN UNIT CELL

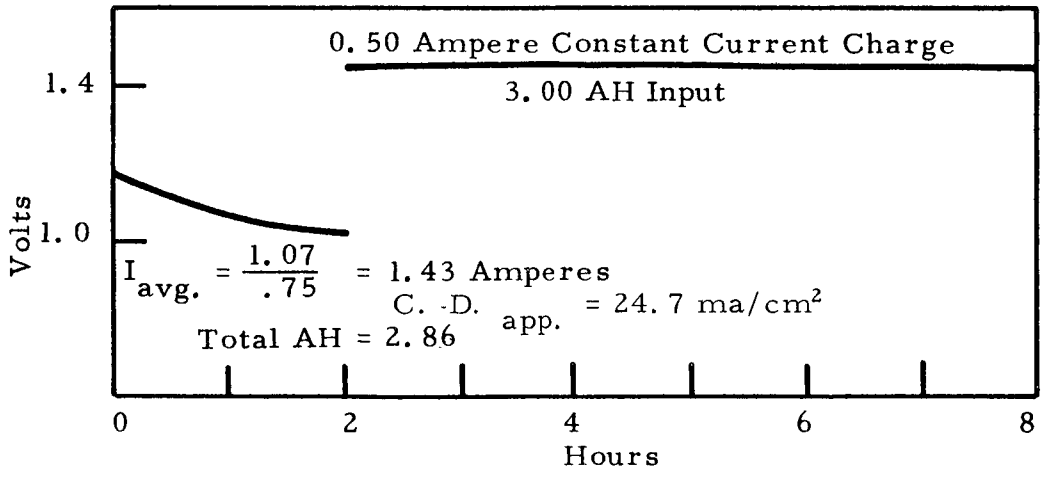

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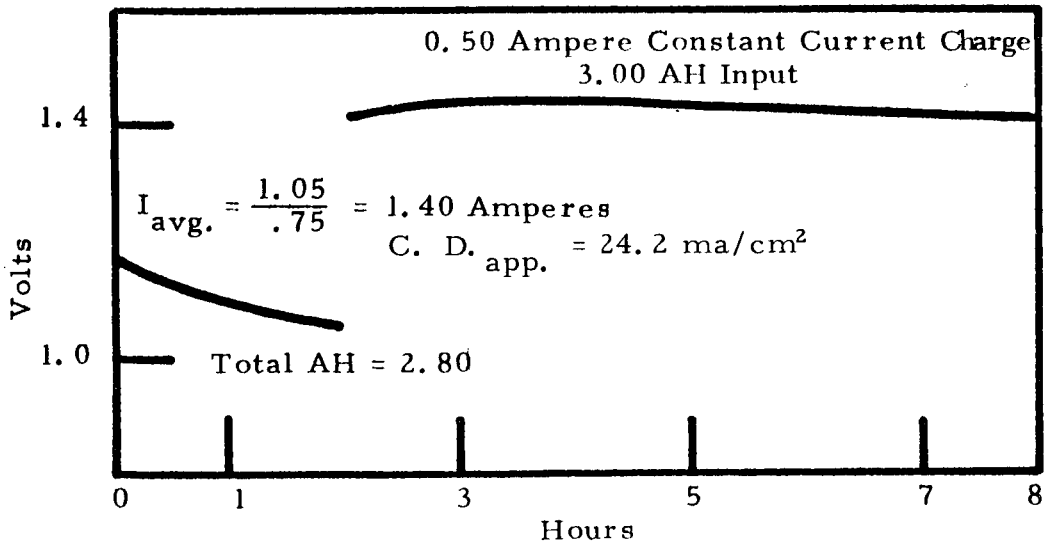
FIGURE 8

14TH DISCHARGE OF ZINC-OXYGEN UNIT CELL



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NEW TECHNOLOGY

There are no new technological advances falling within the scope of this contract to be reported at this time.

PROGRAM FOR NEXT REPORTING INTERVAL

The work planned for the next reporting interval will be directed largely toward continuing the unit cell characterization and optimization studies which were initiated in the present period. This work will be augmented by additional cell performance evaluation over a broader range of current densities. Specific studies will be conducted to optimize the system for the two-hour discharge, two-hour charge cycle as well as the twenty-four hour discharge and twenty-four hour charge cycle. The two-hour discharge, six-hour charge cycle will continue to be used for intermediate charge cycle evaluation. In addition, cell performance will be evaluated as a function of temperature over the range of 0°C to 40°C. Further, work will be initiated in operation of the system under totally sealed conditions.

CONCLUSIONS AND RECOMMENDATIONS

Unit cell work conducted during this quarter has demonstrated that the zinc-oxygen battery system can be successfully recharged. The best results were obtained using an electrolyte of 38% KOH in which 3.5% ZnO had been dissolved. It was also demonstrated that oxidation of the carbon catalyst layer of the "fixed-zone" oxygen electrode which would normally occur when oxygen is evolved electrochemically at this site during charging can be avoided by the use of a separate nickel charging electrode. Constructional changes in the zinc electrode with respect to the use of a more inert restraining member are also recommended. Additionally, it is recommended that the effect of temperature and pressure upon cell operation be investigated.

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